

2

AD-A236 237



OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 400x056yip01&02

DTIC
ELECTE
JUN 04 1991
S C D

Technical Report No. 5

Synthesis of Poly(phenylenes) by a Rapid Polymerization of 1-Bromo-4-lithiobenzene Using HMPA

by

James M. Tour and Eric B. Stephens
Department of Chemistry
University of South Carolina
Columbia, SC 29208



Submission For
DTIC GRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification

Accepted for Publication in

Polymeric Materials Science and Engineering

May 16, 1991

By	
Distribution/	
Availability Codes	
Avail and/or	
Dist	Special
A-1	

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

91-00995



91 6 8 005

REPORT DOCUMENTATION PAGE

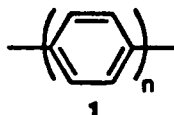
Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report No. 5			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of South Carolina		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION ONR	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Columbia, SC 29208			7b. ADDRESS (City, State, and ZIP Code) Department of Navy Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. N00014-89	PROJECT NO. J-3062	TASK NO.
11. TITLE (Include Security Classification) Synthesis of Poly(phenylenes) by a Rapid Polymerization of 1-Bromo-4-lithiobenzene Using HMPA					
12. PERSONAL AUTHOR(S) James M. Tour and Eric B. Stephens					
13a. TYPE OF REPORT Reprint		13b. TIME COVERED FROM 5/90 TO 5/91		14. DATE OF REPORT (Year, Month, Day) May 16, 1991	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION Polymeric Mater. Sci. Engin. 1991, 64, 233.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Poly(phenylene), aryl-aryl polymerization, HMPA		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A synthesis of poly(phenylene) is described by the treatment of 1-bromo-4-lithiobenzene with hexamethylphosphoramide (HMPA). The polymerization occurred nearly instantaneously even at -78°C. Conditions have been optimized using dioxane as a solvent and HMPA addition at 70-80°C to afford poly(phenylenes) that are predominantly <i>para</i> -linked. The polymers are soluble in THF, dichloromethane, and chloroform. Analysis of the initially formed polymers showed that there was a high bromide content (approximately one bromide for every three aryl rings). Debromination of the material was achieved by treatment with butyllithium and quenching with water. The M_w of the debrominated polymer was 3178 by SEC analysis.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL James M. Tour			22b. TELEPHONE (Include Area Code) (803) 777-9517		22c. OFFICE SYMBOL

SYNTHESIS OF POLY(PHENYLENES) BY A RAPID POLYMERIZATION OF 1-BROMO-4-LITHIOBENZENE USING HMPA

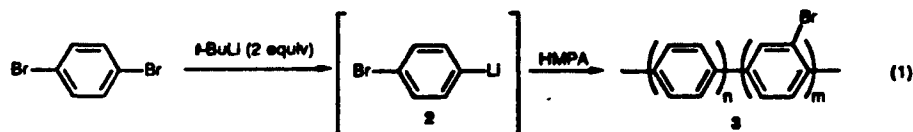
James M. Tour*,¹ and Eric B. Stephens
Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

Poly(*p*-phenylene) (PPP) (1) has attracted much interest since



it can act as an excellent organic conductor upon doping.² The conductivity of doped PPP has reached beyond the semiconducting and into the conducting region with values of $500 \Omega^{-1}\text{cm}^{-1}$ being reported for the pressed pellets (films could not be formed due to the insolubility). There have been numerous syntheses of PPP, however, in nearly all cases, the materials are insoluble and intractable in organic solvents.³⁻¹⁰ The most widely used methods for PPP formation involve the Kovacic and Yamamoto approaches that afford materials with degrees of polymerization of 10-15.²

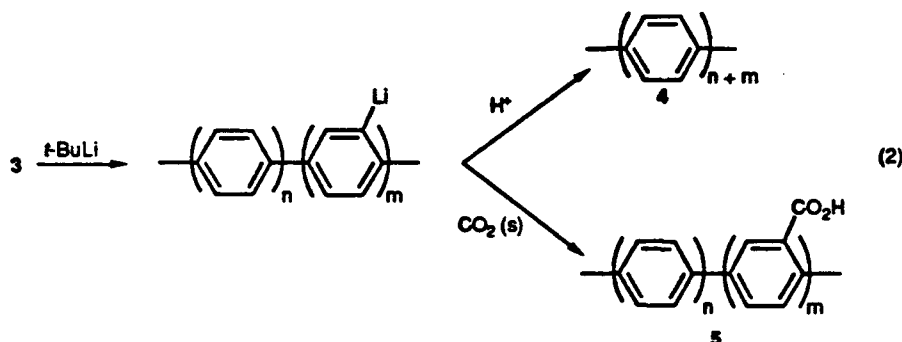
We recently developed a method for the polymerization of 1-bromo-4-lithiobenzene (2) by a facile aryl-aryl coupling scheme which is nearly instantaneous even at -78°C . Though the reaction does occur at -78°C , the optimal method involves the treatment of 1,4-dibromobenzene (1 equiv) in dioxane at 0°C with *t*-butyllithium (2 equiv) to form (2). The intermediacy of 2 was confirmed in a separate experiment by the addition of chlorotrimethylsilane to form 1-bromo-4-(trimethylsilyl)benzene in nearly quantitative yield. The second equivalent of the *t*-butyllithium was necessary for the elimination of the *t*-butyl bromide to afford lithium bromide, isobutylene, and isobutane. This conveniently made all the by-products innocuous. The solution containing 2 was heated to 75°C and hexamethylphosphoramide (HMPA)¹¹ was added all at once. The polymerization to 3 was complete immediately upon completion of the HMPA addition (eq 1). Polymer (3) had one



bromide group (%C, H, Br = 68.94, 4.11, 25.22, respectively) for approximately every three aryl rings in 25-30% yield after one fractional precipitation from ether. It is clear from the FTIR analysis that predominantly *para*-linked material is formed by the strong band at 808 cm^{-1} with weak bands at 882 and 790 cm^{-1} attributed to the *meta*-linkages.¹² Likewise, the

C-Br stretch was evident at 1074 cm^{-1} .⁵ The polymer was soluble in THF, dichloromethane, and chloroform. Though powder X-ray diffraction (XRD) signals have been reported for Kovacic^{2b} and Yamamoto PPP,⁵ no diffraction pattern was observed for **3**, consistent with the solubility of the material. Likewise, scanning electron microscopic (SEM) analysis showed a globular morphology pattern. Size exclusion chromatography (SEC) showed that **3** had a $M_w = 2404$ and $M_w/M_n = 2.33$ relative to polystyrene and oligo(*p*-phenylenes).¹³ There was little, if any, aliphatic material present in the polymer by ^1H NMR.

The brominated polymer **3** could be lithiated with *n*-butyllithium in THF at -78°C and protonated to afford polymer **4** or treated with CO_2 (s) to afford the carboxylated derivative **5** (eq 2). Polymer **4** had 0% bromide content by elemental



analysis. Remarkably, the M_w increased from 2404 for **3** to 3178 for **4** ($M_w/M_n = 2.80$) upon debromination while the material remained soluble with degrees of polymerization >40 . Some possible explanations could be that (1) the bromide content in **3** caused the polymer to be retained more tightly by the SEC columns (cross-linked polystyrene) and thus respond as a lower molecular weight material or (2) re-lithiation caused a further coupling and/or crosslinking of the chains. Again, no powder XRD signals were observable and SEM showed a globular morphology. In the UV spectrum, polymers **3** and **4** showed λ_{max} at 274 and 278 nm, respectively. These values are indicative of mixtures of *para*- and *meta*-linked material.¹⁴ Both polymers **3** and **4** are electroactive. A Pt-electrode was coated with films of both compounds **3** and **4**. Anodic peak potentials (E_{pa}) for the oxidation were at 1.44 and 1.45 V, respectively [recorded relative to Ag/AgNO_3 (0.01 M) in CH_3CN at 50 mV/s scan rate with 0.1 N tetraethylammonium perchlorate (TEAP) as the electrolyte and a Pt working electrode].¹⁵

The formation of polymer **5** demonstrates the flexibility of this approach for the synthesis of functionalized derivatives. The FTIR (KBr) spectrum of **5** was free of the C-Br stretch at 1074 cm^{-1} with the major stretch at 1686 cm^{-1} for the carbonyl moiety. The O-H stretch was weak presumable due to restricted hydrogen bonding in the solid. Elemental analysis showed %C, H = 76.10, 4.99. This procedure could have tremendous applications for the synthesis of functionalized polymers for self-doped conducting systems with fast electrochromic switching times and the fabrication of

Experimental

Preparation of polymer 3. To a 25 mL two-necked round-bottomed flask containing a Teflon coated magnetic stir bar and fitted with a reflux condenser was added 1,4-dibromobenzene (0.477 g, 2.0 mmol) and dioxane (2 mL). After cooling the solution to 0°C, *t*-butyllithium (2.4 mL, 4.2 mmol, 1.75 M in pentane) was slowly added. The ensuing white-yellow slurry was stirred at 0°C for 30 min before warming rapidly to 85°C with an oil bath. To the solution was rapidly added HMPA¹¹ (0.35 mL, 1 mmol) (EXOTHERMIC!) and the dark solution was allowed to cool to room temperature. The reaction mixture was poured into 3 N hydrochloric acid (25 mL) and the organic layer was separated. The aqueous phase was extracted with dichloromethane (3x) and the combined organic phase was washed with 3 N hydrochloric acid (10x). The solution was dried over anhydrous magnesium sulphate and removal of the solvent *in vacuo* afforded a tan-brown solid. Ether soluble fraction = 0.1132 g. Ether insoluble but THF soluble fraction = 0.0296 g. See text for additional data.

Trapping of the intermediate 1-lithio-4-bromobenzene (2) to form 1-bromo-4-(trimethylsilyl)benzene. To a solution of 1,4-dibromobenzene (23.6 g, 100 mmol) in ether (150 mL) was added at -78°C *t*-butyllithium (123.5 mL, 210 mmol, 1.7 M in pentane) over 1 h. The solution was stirred for one hour at -78°C and chlorotrimethylsilane (14 mL, 110 mmol) was added over 10 min. The solution was warmed to room temperature for 30 min and poured into water. The aqueous layer was extracted with ether (3 x 30 mL), and the combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed *in vacuo* and no further purification was needed to afford 19.6 g (86%) of the title compound as a clear colorless oil. IR (neat) 2956, 1574, 1479, 1376, 1251, 1106, 1067, 1012, 841 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.3 Hz, 2 H), 0.24 (s, 9 H).

Debromination of 3 to form 4. To a stirred solution of 3 (0.0329 g) in THF (3.5 mL) was added at -78°C *t*-butyllithium (0.6 mL, 1.0 mL, 1.7 M in pentane). The ensuing brown-black reaction solution was stirred at -78°C for 1 h. To the solution was added at -78°C water (15 mL). The solution was then allowed to warm to room temperature. The solution was then poured into 3 N hydrochloric acid. The organic layer was separated and the aqueous portion extracted with methylene chloride (3x). The combined organic layers were washed with water and dried over magnesium sulphate. Filtration and removal of the solvent *in vacuo* afforded 0.0234 g of a brown solid. See text for additional data.

Acknowledgements

This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), the National Science Foundation (RII-8922165), and the University of South Carolina Venture Fund.

References

(1) Recipient of an Office of Naval Research, Young Investigator Award (1989-92).

(2) For several reviews on the topic, see: a. Kovacic, P.; Jones, M. B. *Chem. Rev.* 1987, 87, 357. b. Noren, G. K.; Stille, J. K. *Macromolec. Rev.* 1971, 5, 385. c. Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. d. Elsenbaumer, R. L.; Schacklette, L. W. in ref 1c. e. Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* 1982, 82, 209.

(3) a. Kovacic, P.; Kyriakis, A. *Tetrahedron Lett.* 1962, 467. b. Kovacic, P. Kyriakis, A. *J. Am. Chem. Soc.* 1963, 85, 454.

(4) Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* 1959, 81, 448.

(5) a. Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull Chem. Soc. Jpn.* 1978, 51, 2091. b. Yamamoto, T.; Yamamoto, A. *Chem Lett.* 1977, 353.

(6) Taylor, S. K.; Bennett, S. G.; Khoury, I.; Kovacic, P. *J. Polym. Sci., Polym. Lett. Ed.* 1981, 19, 85.

(7) a. Fauvarque, J. F.; Petit, M. A.; Pfluger, F.; Jutand, A.; Chevrot, C.; Troupel, M. *Makromol. Chem., Rapid Commun.* 1983, 4, 455. b. Froyer, G.; Maurice, F.; Goblot, J. Y.; Fauvarque, J. F.; Petit, M. A.; Digua, A. *Mol. Cryst. Liq. Cryst.* 1985, 118, 267. c. Favarque, J. F.; Digua, A.; Petit, M. A.; Savard, J. *Makromolec. Chem.* 1985, 186, 2415.

(8) Ballard, D. G. H.; Curtis, A.; Shirley, I. M.; Taylor, S. *C. J. Chem. Soc. Chem. Commun.* 1983, 954.

(9) a. Stille, J. K.; Gilliams, Y. *Macromolecules* 1971, 4, 515. b. Vankerckhoven, H. F.; Gilliams, Y. K. Stille, J. K. *Macromolecules* 1972, 5, 541.

(10) a. Goldfinger, G. *J. Polym. Sci.* 1949, 4, 93. b. Edwards, G. A.; Goldfinger, G. *J. Polym. Sci.* 1955, 16, 589.

(11) *Caution*: HMPA is a highly toxic cancer suspect agent. All manipulations with this material should be carried out in a well ventilated hood and rubber gloves should be worn.

(12) Kovacic, P.; Marchiona, V. J.; Koch, F. W.; Oziomek, J. *J. Org. Chem.* 1966, 31, 2467.

(13) The oligo(*p*-phenylene) standards used were biphenyl, *p*-triphenyl, *p*-quaterphenyl, and *p*-sexiphenyl with a correlation between the four standards of ≥ 0.997 . The M_w values for our materials using oligo(*p*-phenylene) standards was very close to the values obtained with polystyrene standards.

(14) Ried, W.; Freitag, D. *Angew. Chem. Int. Ed. Engl.* 1968, 7, 835.

(15) Diaz, A.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electroanal. Chem.* 1981, 121, 355.

(16) a. Patil, A. O.; Ikenoue, Y.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* 1987, 20, 151. b. Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* 1987, 109, 1858. c. Ikenoue, Y.; Chiang, J.; Patil, A.O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* 1988, 110, 2983. d. Ikenoue, Y.; Uotani, N.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Synth. Met.* 1989, 30, 305. e. Havinga, E.; van Horsen, L.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *Polym. Bull.* 1987, 18, 277. f. Tsai, W.; Jang, G. W.;

Rajeshwar, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1776. g.
Shi, S.; Wudl, F. *Macromolec.* **1990**, *23*, 2119.